Use of Diode Analogy in Explaining the Voltammetric Characteristics of Immobilized Ferrocenyl Moieties on a Silicon Surface

AUTHOR(S):

Herrera, Marvin U.; Ichii, Takashi; Murase, Kuniaki; Sugimura, Hiroyuki

CHEMELECTROCHEM COMMUNICATIONS

ChemPubSoc Europe

DOI: 10.1002/celc.201((will be completed by the editorial staff))

Use of diode analogy in explaining the voltammetric characteristics of immobilized ferrocenyl moieties on a Si surface

Marvin U. Herrera*[a], Takashi Ichii[a], Kuniaki Murase[a], Hiroyuki Sugimura *[a]

Dedication ((optional))

Abstract Text. The creation of a model that explains the dependency of the voltammetric characteristics of ferrocene-terminated Si (Si-Fc) samples on the type of substrate (n- or p-type) would be helpful in understanding the electronic characteristics of these materials. To explain the dependency, Si-Fc samples are treated like diodes. As diodes, the samples may allow charge flow in a certain direction while inhibiting the opposite flow. The treatment of a sample as a diode is done to facilitate analysis of charge flow within the sample, thus enabling easy prediction of its electrochemical characteristics. Likewise, the trend of the anodic peak potential versus light intensity plot (of the samples with n-type substrate) was also associated with the sample's diode characteristics. Our proposed model opens many scientific possibilities, especially in relating the voltammetric characteristics of electroactive molecules on a Si surface with the properties of a diode (e.g., open-circuit voltage).

Ferrocene-containing moieties on semiconductor or semiconductor oxide surfaces have been the subject of many reports [1-22] and have potentials as memory devices [6,12,13,17]. The Fe atom in the ferrocenyl (Fc) moiety has two stable and reversible oxidation states. Its oxidation state can increase from +2 to +3 upon the introduction of potential and return back to +2 when it is removed. These two reversible oxidation states could correspond to the bits of memory devices. However, the electrochemical characteristics of Fc-terminated Si (Si-Fc) depend on whether the silicon substrate is n-type or p-type. Cyclic voltammetry (CV) measurements of Si-Fc samples with an n-type substrate (n Si-Fc) show the presence of cathodic and anodic peaks only when the measurements are done under illumination [4,6,8,18]. This is in contrast with those with a p-type substrate (p Si-Fc), which show the presence of cathodic and anodic peaks with or without illumination. We believe that the creation of a model that can describe these phenomena would lead to a better understanding of the electronic properties of these materials and this could be very helpful in the construction of molecular memory devices.

[a] *Dr. Marvin U. Herrera, Prof. Takashi Ichii, Prof. Kuniaki Murase, Prof. Hiroyuki Sugimura*
Department of Materials Science and Engineering
Kyoto University
Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: hiroyuki-sugimura@mtl.kyoto-u.ac.jp
[b] *Dr. Marvin U. Herrera (present address)*
Institute of Mathematical Sciences and Physics
University of the Philippines Los Banos
College, Laguna, 4031, Philippines
E-mail: muherrera@uplb.edu.ph

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.20xxxxxxx.((Please delete if not appropriate))

For n Si-Fc samples in the dark, the depletion condition [6,8,18] existing within the sample has been associated to the absence of anodic and cathodic peaks during CV measurements. Meanwhile, the occurrence of CV peaks on p Si-Fc samples with or without illumination has been related to accumulation condition. Both the depletion and accumulation conditions are consequences of the bending of energy bands due to an applied bias and are related to the existence of a potential barrier at the Si substrate-molecular layer interface (in the equilibrium condition). To be able to construct a more holistic model, we generalized that the cause of the above phenomenon is the existence of a potential barrier at the Si-molecular layer interface, which makes the sample behave like a diode in the presence of an external bias (e.g. CV measurements). Because diodes have already been well studied, the available information about them could be used to understand the flow of charges within Si-Fc samples, and thus could lead to a better understanding of the electrochemical characteristics of the samples.

A Si-Fc sample, which is connected to a cyclic voltammetry set-up, is treated like a diode with external bias. The diode-like characteristics (e.g., current in one direction flows with greater ease than the opposite direction) of the molecular layer on a semiconductor surface have been cited in the literature [23-32]. The exact nature of the diode that can best describe the Si-Fc sample (e.g., Schottky diode, tunnel diode) is beyond the scope of this report. With respect to our proposed model, our primary concern relates to the characteristics of a diode that allow charge flow in a certain direction while inhibiting the opposite direction.

Cyclic voltammetry (CV) can be used to determine the electrochemical characteristics of Si-Fc samples. During CV measurements, the substrate of the Si-Fc sample is connected to the working electrode, while the Fc-containing layer faces the counter and reference electrodes. For simplicity, we could take the counter and reference electrodes as a single entity and their potential is taken as the reference. During measurements, the bias in the working electrode is increased and is decreased with a specified scan rate in a cyclic manner.

Figure 1 shows the energy band diagram of p Si-Fc and n Si-Fc samples in a CV set-up and placed in the dark. The figures show the schematics of the valence band (E_V), conduction band (E_c) and Fermi energy (E_F) of the samples. Since the substrate is Si, the difference between the valence and conduction band (band gap) is 1.12 eV. The Si substrate is connected to an external bias while the Fc-containing layer faces the reference potential. Figures 1(a) and 1(c) are energy band diagrams of the samples when the applied bias is zero. In this condition, the Fermi energy (E_F) is the same throughout the sample. For the p Si-Fc sample, some of the electrons from the bulk Si gather near the interface (beneath the Si surface),

CHEMELECTROCHEM
COMMUNICATIONS
www.chemelectrochem.org

creating a downward bending of the conduction (E_c) and valence (E_v) energy bands. Meanwhile, for the n Si-Fc sample, some of the holes from the bulk Si gather near the interface (beneath the Si surface), creating an upward bending of the energy bands. For both samples, the bending of the energy bands creates a potential barrier, which is responsible for their diode-like behaviors.

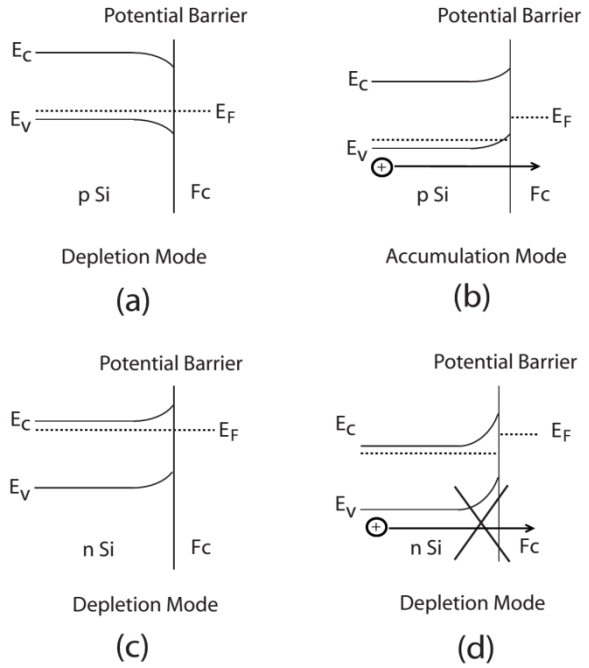


Figure 1. Energy band diagram of Si-Fc samples, which are placed in the dark. The Si substrate is connected to the working electrode while the Fc-containing layer faces the counter and reference electrodes. The diagrams in the upper portion are p Si-Fc samples having (a) a zero applied bias and (b) a positive external bias connected to the Si substrate. The diagrams in the lower portion (c,d) are the n-type counterparts of those of a,b.

The presence of an anodic peak is associated with an increase in the Fe oxidation states to +3. To increase the Fe oxidation state, holes must be available in the Fc-containing layer (or in another view, electrons must move from the Fc layer to Si substrate). Holes from the voltage source should move towards the Si substrate, cross the Si-molecular layer interface, move into the molecular layer and into the Fc moieties. However, the potential barrier in the Si-molecular layer interface (depending on its nature and amount of external bias) could either allow or inhibit the passage of holes to the Fc-containing layer. It is possible that both holes and electrons move across the potential barrier. However, it would just be sufficient to describe the hole flow because the direction of electron flow can be viewed as its opposite (e.g., an electron moving from the Fc layer to the Si substrate can be viewed as a hole moving from the Si substrate to the Fc layer). In p Si-Fc samples (in the dark), the placement of a sufficiently high positive bias can change the bending configuration to an accumulation mode (figure 1(b)), thus allowing the holes to move to the molecular layer. This situation is analogous to a diode in the forward bias condition (figure 2(b)). Meanwhile, for the n Si-Fc sample (in the dark), the placement of positive bias can further deepen the depletion layer (figure 1(d)); therefore, the holes are inhibited from moving to the molecular layer. This situation is analogous to a diode in reversed bias mode (figure 2(d)).

The presence of a cathodic peak is associated with a decrease in the Fe oxidation state back to +2. This decrease is associated with the detachment of acquired holes from the Fc moieties. The decrease in the Fe oxidation state back to +2 will only occur, if it was first increased to +3. Depending on the nature of the potential barrier, the detached holes may either lump near the interface or go back to the Si substrate. For example, in the case of p Si-Fc samples (in the dark), the existence of a potential barrier inhibits the transfer of holes from the molecular layer back to the Si substrate when the applied potential is lowered. Instead, the detached holes can gather near the Si-molecular interface (side of the molecular layer) and further strengthen its hindrance to the passage of holes. This condition is analogous to a diode in reverse bias mode (figure 2(a)). Meanwhile, for p Si-Fc and n Si-Fc samples under sufficient illumination, the transfer of detached holes from the molecular layer back to the Si substrate is possible when the applied potential is lowered. These conditions are analogous to diodes in reverse bias (figure 2(e)) and forward bias (figure 2(g)) modes, respectively.

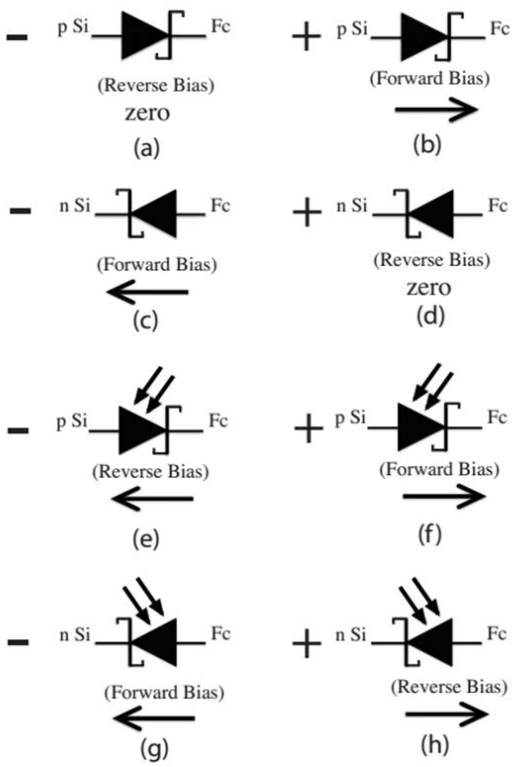


Figure 2. Si-Fc samples in the dark (a-d) and under illumination (e-h), which are treated like diodes. The terms "-" and "+" denote the applied potential with respect to the opposite side. The arrow indicates the direction of the movement of holes, which could be zero. The items in parentheses denote the biasing condition of the Si-Fc samples.

Treating the sample as a diode allows easier identification of the allowable direction of hole flow across the substrate-molecular interface. Figure 2 shows the different types of samples, which are represented as diodes. Figures 2(a)-2(d) represent samples that are placed in the dark while figures 2(e)-2(h) represent samples that are illuminated. The

amount of bias, which is applied to the Si substrate, is classified either as lower (-) or higher (+) potential with respect to the opposite side of the sample (which is treated as a reference). The biasing mode of the sample (as indicated in parentheses) could either be “reverse bias” or “forward bias”. The allowable directions of hole flow (as indicated by an arrow) at a specific biasing mode could either be (1) to the Si substrate, (2) to the Fc-containing layer or (3) none. The figure uses the symbol for a Schottky diode because it could be the closest possible analogy for the Si-Fc samples. It is notable that figure 2 suggests that the flow of holes to the molecular layer in p Si-Fc samples (in the dark and under illumination) at high potential is due to the forward bias current (figure 2(b), 2(f)), while for that of the n Si-Fc samples (under illumination) is due to the reversed bias current (figure 2(h)).

Table 1. Direction of hole movements of the different Si-Fc samples based on the diode configurations in figure 2.

Sample	Direction of hole movements		Increase Fe oxidation state to +3?
	Lower potential	Higher potential	
p Si-Fc (dark)	no flow [a]	Fc	Yes
n Si-Fc (dark)	Si substrate	no flow [a]	No
p Si-Fc (light)	Si substrate	Fc	Yes
n Si-Fc (light)	Si substrate	Fc	Yes

[a] “no flow” means that the holes stay on the Si substrate

Table 1 summarizes the directions of hole flow of the different samples (at a specific biasing condition) that were presented in figure 2. All samples, except that of the n Si-Fc sample in the dark, allow hole transfer from the Si substrate to the Fc-containing layer when the applied potential is changed from low to high potential. For these types of samples, holes are available in the Fc-containing layer, making it possible for the Fe oxidation state to increase to +3. Thus, the anodic peak and its accompanying cathodic peak could be seen during CV measurements. Meanwhile, for n Si-Fc samples in the dark, the holes stay at the Si substrate even if the applied potential is increased. In this condition, the oxidation states of the Fc moieties in the molecular layer cannot increase, so no peaks appear during CV measurements.

For n Si-Fc samples, illumination is needed in order to start the movement of holes to the Fc-containing layer. CV peaks only appear in the presence of sufficient illumination. This condition is analogous to that of a photodiode (or solar cell) in a reversed bias condition (figure 2(h)). As such, illumination creates electron-hole pairs, which split into free electrons and free holes in the depletion region. After splitting, the holes go to the Si surface and into the Fc-containing layer, which can increase the Fe oxidation state to +3.

Figure 3 shows the cyclic voltammograms of the n Si-Fc sample measured at different illumination intensities with a scan rate of 0.5 V/s. At illumination intensities of 5, 10, 20, 30 mW-cm^2, the differences between the anodic and cathodic peak potentials are 23, 14, 11, 7 mV, respectively. The said differences are small, thus these imply that the electrochemical process happening in the sample is reversible. Meanwhile, figure 4 shows the plot of their anodic peak potential as a function of light intensity. The figure shows the anodic peak position shift to a lower potential when the illumination intensity was increased until it saturated. The anodic peak potential of the sample correlates with the onset of the reverse bias current or the potential in which holes start to move to the Fc-containing layer. This potential is also the transition point from forward bias mode to reverse bias mode. The shift in the anodic peak to a lower potential with an increase in illumination intensity (figure 4) is thought to be the effect of the lowering of the potential needed to trigger the onset of reversed bias current due to the effect of illumination. This is compatible with the characteristics of photodiodes or solar cells, in which the transition point from the reversed bias mode to forward bias mode or open-circuit voltage [33-36] shifts to a higher potential when the illumination intensity is increased. The opposite in the shift movements (of the open-circuit voltage and the anodic peak) is simply due to the difference in the placement of the reference potential in I-V measurements (which is used in determining the open-circuit voltage) and in CV measurements (which is used in determining anodic peak position). In I-V measurements, the reference potential is placed at the Si substrate (or base of the diode) while in CV measurements; the molecular layer (or side intended to be illuminated) faces the reference potential. (Note also that the CV peak potential is associated with a transition from forward to reverse bias mode, and this is opposite to that of an open-circuit which is associated with the transition from reverse to forward bias mode.) Figure 4 also shows that the value of the peak potential tends to saturate at high illumination intensity. This is analogous with the tendency of the change in open circuit voltage [33-36] to become smaller at high light intensity. The parallelism between the behavior of the anodic peak position (of an n Si-Fc sample) and open circuit voltage (of a photodiode or solar cell) with the increase in illumination intensity supports the notion that the voltammetric characteristics of the sample are affected by its diode nature.

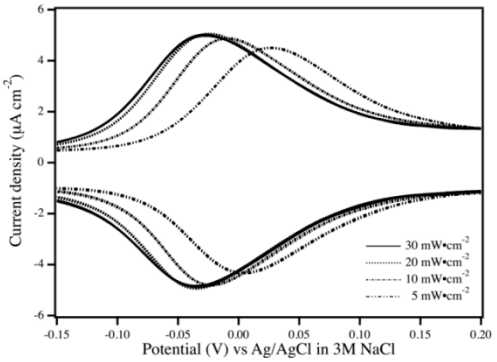


Figure 3. Cyclic voltammogram of the n Si-Fc sample at different illumination intensities measured at room temperature with a scan rate of 0.5 V/s.

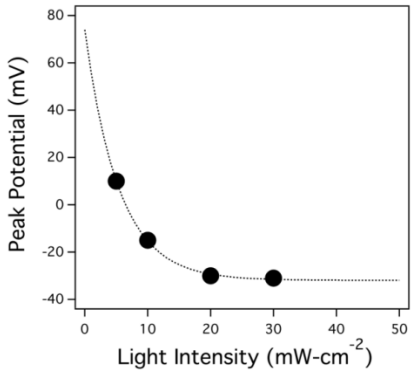


Figure 4. Light intensity vs. anodic peak potential of an n Si-Fc sample. The dashed line represents the trend of the plotted points. For presentation purposes, the trend was extrapolated up to zero light intensity even if no anodic peak was associated with it.

In summary, our proposed model relates the dependency of the absence or presence of anodic and cathodic peaks during CV measurements on the type of substrate with the existence of a potential barrier, which can affect the flow of holes to the Fc-containing layer. We treated Si-Fc samples as diodes to facilitate our analysis on the allowable direction of hole flow within the sample. The analysis of the allowable direction of hole flow was done to determine if holes were available at the Fc-containing layer to increase its oxidation state. Likewise, we also associated the shifting of the anodic peak potential of the n Si-Fc sample (with changes in illumination intensity) with its diode properties.

Our model shows how the diode characteristics of a molecular layer on a semiconductor substrate affect the movement of charges within the sample, thus affecting the outcome of CV measurements. This not only offers a better understanding of the electrochemical characteristics of Si-Fc samples, but also creates many scientific opportunities, especially in relating the voltammetric characteristics of electroactive molecules on a Si surface with the different characteristics of diodes. This information will be helpful in creating molecule-based memory devices.

Experimental Section

The n Si-Fc samples were prepared using a photochemical technique using vinylferrocene as a precursor and dibutyl ether as a grafting medium. The preparation involved the illumination of a hydrogen-terminated Si(111), which was immersed in vinylferrocene-dibutyl ether solution under visible light. The substrate that was used in this study was a single-sided, mirror-polished, and phosphorus-doped (n-type) Si(111). The substrate had resistivity of around 1-10 Ω-cm. Details about the preparation have been presented elsewhere [9]. A conventional three-electrode set-up, which was connected to an electrochemical analyzer, was used for the CV measurements. The measurements were made at room temperature under visible light illumination with different intensities. A 0.1M $HClO_4$ solution was used as the electrolyte. The electrolyte was bubbled prior to and during the measurements to remove oxygen molecules in the solution. The n Si-Fc sample was connected at the working electrode. To established ohmic contact between the copper plate (which was connected to the working electrode) and scratched backside of the substrate, a gallium-indium eutectic was placed between them. Insulating epoxy resin was placed on the whole backside and lateral side of the substrate to electrically insulate them during CV measurements. In this condition, only the front side of the sample was active during measurements. A platinum coil was used as the counter electrode. An Ag/AgCl electrode, which was immersed in 3.0 M NaCl, was used as a reference electrode. Its potential was 0.226 ± 0.004 V versus a standard hydrogen electrode (SHE).

Keywords: ferrocene-terminated silicon • self-assembled monolayer • diode• interfaces • voltammetry

[1] S. Ciampi, P.K. Eggers, G. Le Saux, M. James, J.B. Harper, J.J. Gooding, *Langmuir* **2009**, *25*, 2530-2539.
[2] S. Ciampi, G. Le Saux, J.B. Harper and J.J. Gooding, *Electroanalysis* **2008**, *20*, 1513-1519.
[3] M. Cossi, M.F. Iozzi, A.G. Marrani, T. Lavecchia, P. Galloni, R. Zanoni F. Decker, *J. Phys. Chem. B* **2006**, *110*, 22961-22965.
[4] E. A. Dalchiele, A. Aurora, G. Bernardini, F. Cattaruzza, A. Flamini, P. Pallavicini, R. Zanoni, F. Decker, *J. Electroanal. Chem.* **2005**, *579,* 133-142.
[5] F. Decker, F. Cattaruzza, C. Coluzza, A. Flamini, A.G. Marrani, R. Zanoni, E.A. Dalchiele, *J. Phys. Chem. B* **2006**, *110*, 7374-7379.
[6] B. Fabre, *Acc. Chem. Res.* **2010**, *43*, 1509-1518.
[7] B. Fabre, F. Hauquier, *J. Phys. Chem. B.* **2006**, *110*, 6848-6855.
[8] S. Gowda, G. Mathur, V. Misra, *Appl. Phys. Lett.* **2007**, *90*, 142113-1 - 3.
[9] M. Herrera, T. Ichii, K. Murase, H. Sugimura, *Chem. Lett.* **2012**, *41*, 1188-1190.
[10] K. Huang, F. Duclairoir, T. Pro, J. Buckley, G. Marchand, E. Martinez, J.-C. Marchon, B. De Salvo, G. Delapierre, F. Vinet, *ChemPhysChem* **2009**, *10*, 963-971.
[11] P. Kruse, E.R. Johnson, G.A. DiLabio, R.A. Wolkow, *Nano Lett.* **2002**, *2*, 807-810.
[12] Q. Li, G. Mathur, M. Homsi, S. Surthi, V. Misra, V. Malinovskii, K.-H. Schweikart, L. Yu, J.S. Lindsey, Z. Liu, R.B. Dabke, A. Yasseri, D.F. Bocian, W.G. Kuhr, *Appl. Phys. Lett.* **2002**, *81*, 1494-1496.
[13] Q. Li, S. Surthi, G. Mathur, S. Gowda, V. Misra, T.A. Sorenson, R.C. Tenent, W.G. Kuhr, S. Tamaru, J.S. Lindsey, Z. Liu, D.F. Bocian, *Appl. Phys. Lett.* **2003**, *83,* 198-200.
[14] M. Lu, T. He, J.M. Tour, *Chem. Mater*. **2008**, *20*, 7352-7355.
[15] A.G. Marrani, E.A. Dalchiele, R. Zanoni, F. Decker, F. Cattaruzza, D. Bonifazi, M. Prato, *Electrochim. Acta* **2008**, *53*, 3903-3909.
[16] A.G. Marrani, F. Cattaruzza, F. Decker, P. Galloni, R. Zanoni, *Superlattices Microstruct.* **2009**, *46*, 40-43.
[17] K.M. Roth, A.A. Yasseri, Z. Liu , R.B. Dabke, V. Malinovskii, K.-H. Schweikart, L. Yu, H. Tiznado, F. Zaera, J.S. Lindsey, W.G. Kuhr, D.F. Bocian, *J. Am. Chem. Soc.* **2003**, *125,* 505-517.
[18] H. Sano, M. Zhao, D. Kasahara, K. Murase, T. Ichii, H. Sugimura, *J. Colloid Interface Sci.* **2011,** *361*, 259-269.
[19] N. Tajimi, H. Sano, K. Murase, K.-H. Lee, H. Sugimura, *Langmuir* **2007**, *23*, 3193-3198.
[20] R. Zanoni, F. Cattaruzza, C. Coluzza, E.A. Dalchiele, F. Decker, G. Di Santo, A. Flamini, L. Funari, A.G. Marrani, *Surf. Sci.* **2005,** *575,* 260-272.
[21] R. Zanoni, A. Aurora, F. Cattaruzza, C. Coluzza, E.A. Dalchiele, F. Decker, G. Di Santo, A. Flamini, L. Funari, A.G. Marrani, *Mater. Sci. Eng., C* **2006,** *26,* 840-845.
[22] R. Zanoni, M. Cossi, M.F. Iozzi, F. Cattaruzza, E.A. Dalchiele, F. Decker, A.G. Marrani, M. Valori, *Superlattices Microstruct.* **2008,** *44,* 542-549.
[23] E.J. Faber, L.C.P.M. de Smet, W. Olthuis, H. Zuilhof, E.J.R. Sudholter, P. Bergveld, A. van den Berg, *ChemPhysChem* **2005**, *6*, 2153 – 2166.
[24] R.K. Hiremath, B.G. Mulimani, M.K. Rabinal, I.M. Khazi, *J. Phys.: Condens. Matter* **2007**,*19*, 446003-1 -12.
[25] R.K. Hiremath, M.K. Rabinal, B.G. Mulimani, I.M. Khazi, *Langmuir* **2008**, *24*, 11300-11306.
[26] S. Maldonado, K.E. Plass, D. Knapp, N.S. Lewis, *J. Phys. Chem. C* **2007**, *111*, 17690-17699.
[27] A. Salomon, T. Bocking, J.J. Gooding, D. Cahen, *Nano Letters* **2006**, *6*, 2873-2876.
[28] A. Scott, D.B. Janes, C. Risko, M.A. Ratner, *Appl. Phys. Lett.* **2007**, *91*, 033508-1 -3 .
[29] A. Vilan, O. Yaffe, A. Biller, A. Salomon, A. Kahn, D. Cahen, *Adv. Mater.* **2010**, *22*, 140–159.
[30] O. Yaffe, L. Scheres, S.R. Puniredd, N. Stein, A. Biller, R.H. Lavan, H. Shpaisman, H. Zuilhof, H. Haick, D. Cahen, A. Vilan, *Nano Letters* **2009**, *9*, 2390-2394.
[31] F. Yakuphanoglu, *Synthetic Metals* **2007**, *157*, 859–862.
[32] F. Yakuphanoglu, S. Okur, H. Ozgener, *Microelectronic Engineering* **2009**, *86*, 2358–2363.
[33] R. Boylestad, L. Nashelsky, *Electronic devices and circuit theory 10th Ed.*, Pearson Prentice Hall, United States of America **2009** p 823.
[34] M. Chegaar, A. Hamzaoui, A. Namoda, P. Petit, M. Aillerie, A. Herguth, *Energy Procedia* **2013**, *36*, 722-729.
[35] E. Cuce, P.M. Cuce, T. Bali, *Appl. Energy* **2013**, *111*, 374-382 .

CHEMELECTROCHEM COMMUNICATIONS
ChemPubSoc Europe

[36] F. Khan, S.N. Singh, M. Husain, *Sol. Energy Mater. Sol Cells* **2010**, *94*, 1473-1476.

Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

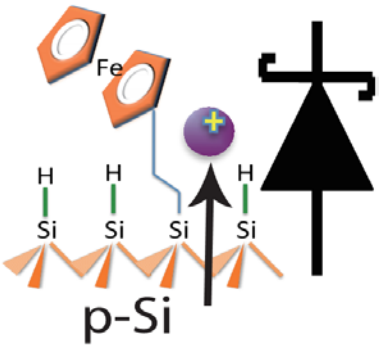
CHEMELECTROCHEM
COMMUNICATIONS
www.chemelectrochem.org

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATIONS

The ferrocene-terminated Si samples were treated like diodes. The diode nature of the samples was attributed to the existence of a potential barrier between the Si substrate and the ferrocene layer. The said diode nature of the samples was used to explain some of its characteristics such as the dependency of its cyclic voltammetry response with type of substrate and illumination.



Marvin U. Herrera, Takashi Ichii, Kuniaki Murase, Hiroyuki Sugimura**

Page No. – Page No.

Use of diode analogy in explaining the voltammetric characteristics of immobilized ferrocenyl moieties on a Si surface